TECHNICAL NOTE

D-1559

EFFECT OF COMPOSITION ON COMBUSTION

OF SOLID PROPELLANTS DURING A

RAPID PRESSURE DECREASE

By Carl C. Ciepluch

Lewis Research Center
Cleveland, Ohio

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

WASHINGTON   December 1962

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

TECHNICAL NOTE D-1559

EFFECT OF COMPOSITION ON COMBUSTION

OF SOLID PROPELLANTS DURING A

RAPID PRESSURE DECREASE

By Carl C. Ciepluch

SUMMARY

The response of solid-propellant combustion to a pressure transient was studied in an apparatus that could be vented at a variable rate. The principal measurement was the time required for the pressure to decrease to one-half its initial value. The data are presented and discussed in terms of τ, the maximum value of the time required to extinguish combustion. The value of τ was decreased by an increase in aluminum or ammonium perchlorate concentration and was increased by an increase in binder concentration. An increase in the average particle size of ammonium perchlorate resulted in a decrease in τ. The addition of aluminum oxide produced a decrease in the value of τ, while the addition of potassium fluoride increased it.

The results indicate that the ease with which solid-propellant combustion may be extinguished is strongly dependent on physical factors such as the average size and the thermal conductivity of solid particles contained in the propellant. Analysis of the results suggested that hot-particle retention at the surface of the propellant was a major cause of the continuance of combustion in a rapidly decreasing pressure field. An examination of the data also indicated no correlation between τ and the propellant-strand burning rate.

INTRODUCTION

An investigation is being conducted at the Lewis Research Center on the behavior of solid-propellant flames during pressure transients. The initial phase of this investigation has been concerned with the point where the flame is extinguished as a result of a pressure decay transient. Reference 1 states that there is a discrete rate of pressure decay above which a solid-propellant flame cannot exist and is consequently extinguished. Although the flame may disappear momentarily below this rate of pressure decay, the combustion process recovers and continues at a new steady-state rate. This report deals with the effect of propellant composition on the pressure decay rate required to just extinguish combustion. Propellant composition variables such as binder type and concentration,

oxidizer particle size and concentration, and various inert or reactive additives were studied.

APPARATUS AND PROPELLANTS

The experimental apparatus was the same as that described in detail in reference 1. The propellant charge was a slab 3 by 5 by 1 inch. A rectangular chamber (fig. 1) that contained a nozzle encased the propellant. A quick-opening chamber vent was used to decrease the chamber pressure suddenly. The venting pressure was one-thirtieth of atmospheric pressure. The rate at which the chamber pressure diminished was varied by varying the size of the vent orifice. To measure the variation in chamber pressure, a high-frequency-response pressure transducer was employed, and the variation of combustion luminosity was measured when required through a quartz window.
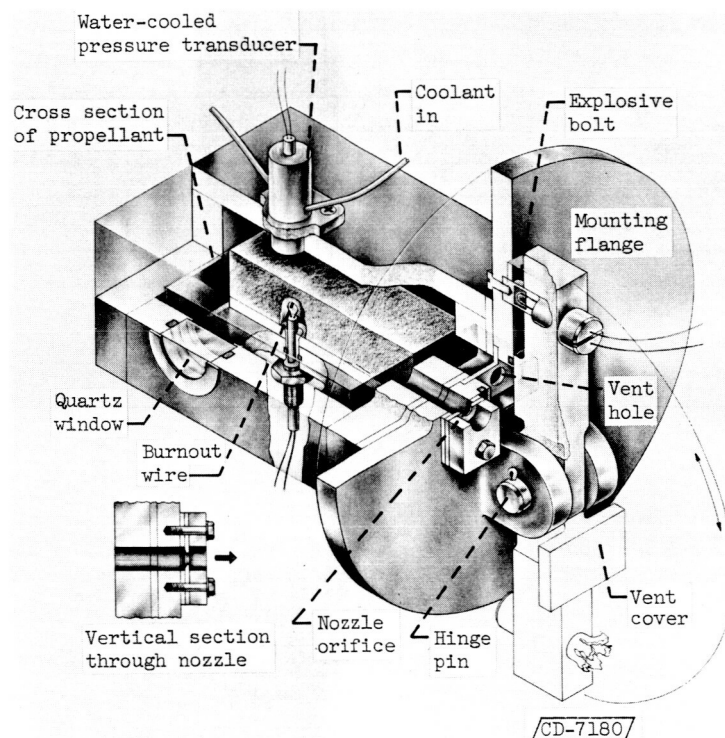
Figure 1. - Combustion-chamber assembly.

Since the rate of chamber-pressure decrease varied during the venting process, it was convenient to represent the rate of pressure change by the length of time required to produce a given change in pressure. This time Δt was defined as the length of time required to reduce the chamber pressure P by

50 percent. The rate of pressure change was therefore inversely proportional to Δt; that is,

$$\frac{\Delta P_{50}}{\Delta t} = \frac{1}{2} \frac{P}{\Delta t}$$

The maximum value of Δt for which combustion is just extinguished is called τ and it was found by a cut-and-try process. A minimum of four runs was required to bracket τ to within ±3 percent for each propellant composition.

TABLE I. - PROPELLANT COMPOSITIONS AND COMBUSTION CHARACTERISTICS

Binder		Oxidizer			Additive		Strand burning rate r (at 500 lb/sq in. abs), in./sec (b)	K	n
Type	Weight percent	Weight percent	Blend, percent (a)	Type	Weight percent			
PBAA[c]	24.8	75	70 C, 30 F	--------	-----	0.2207	0.00585	0.584
	18.8	81	70 C, 30 F	--------	-----	.2632	.0593	.240
	13.8	86	70 C, 30 F	--------	-----	.355	.0745	.251
	18.8	79	70 C, 30 F	Aluminum	2	.278	.0447	.294
	18.8	72	77 C, 23 F	Aluminum	9	.263	.0324	.337
	18.8	72	70 C, 30 F	Aluminum	9	----	-----	----
	13.8	76.6	70 C, 30 F		9.4	.310	.0155	.482
	18.8	65	85 C, 15 F		16	.2413	.0395	.2915
	18.8	72	100 F		9	.643	.0364	.462
	18.8	72	100 C		9	.246	.00432	.650
	15.8	81	70 C, 30 F	Aluminum oxide (F)	3	.364	.0457	.334
	15.8	81	70 C, 30 F	Aluminum oxide (C)	3	.387	.0603	.299
	15.8	81	70 C, 30 F	Potassium fluoride (F)	3	.315	.0654	.253
	15.8	81	70 C, 30 F	Potassium fluoride (C)	3	.319	.0330	.365
PU[d]	19.0	72	77 C, 23 F	Aluminum	9	----	-----	----

[a]Coarse, C; fine, F.

[b]Burning rate $r = KP^n$, where K is a constant, P is pressure, and n is the burning-rate exponent.

[c]Epoxy-cross-linked copolymer of butadiene and a carboxylic monomer. (All PBAA propellants contained approximately 0.2 percent magnesium oxide.)

[d]A polyurethane.

A listing of the propellant compositions that were investigated is shown in table I. Two propellant binders were used in this investigation; one (PBAA) was an epoxy-cross-linked copolymer of butadiene and a carboxylic monomer, and the other (PU) was a polyurethane. The ammonium perchlorate oxidizer consisted of a blend of fine and coarse powders, as noted in table I. The fine ammonium perchlorate powder had a 50-percent-weight average particle size of 11 microns, while the coarse ammonium perchlorate averaged 89 microns. The 50-percent-weight average particle size of the aluminum powder additive was 6.7 microns. Anhydrous aluminum oxide powders had 50-percent-weight particle sizes of 5 and 64 microns for fine and coarse blends, respectively. The potassium fluoride averaged 6.6 microns for the fine blend and 110 for the coarse. Particle-size distributions were obtained with a micromerograph. Included in table I are values of burning rate r determined for each propellant in a conventional strand burner at a pressure of 500 pounds per square inch absolute. Also given are values of the constant K and the burning-rate exponent n calculated from the equation $r = KP^n$, where P is the chamber pressure, which was varied from 400 to 1000 pounds per square inch absolute.

RESULTS

A comparison of typical measured and calculated pressure decay transients that were obtained by a sudden increase in nozzle discharge area is shown in figure 2. Pressure transients for two cases were calculated by the method given in
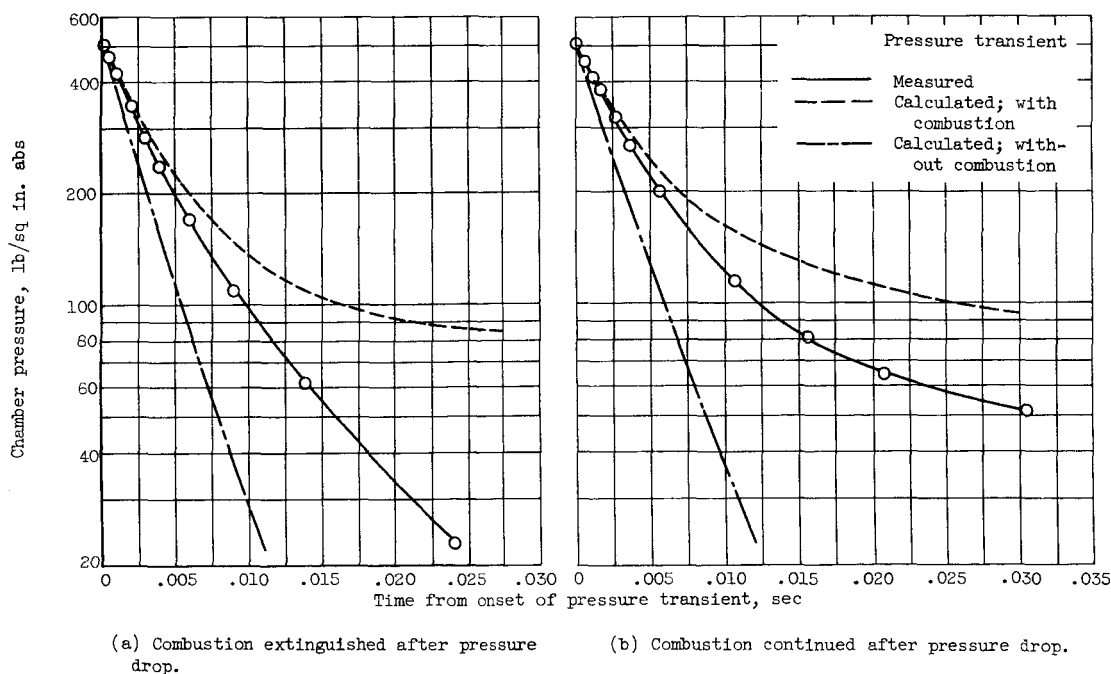

(a) Combustion extinguished after pressure drop.

(b) Combustion continued after pressure drop.

Figure 2. - Comparison of measured and calculated pressure decay transients.

4

the appendix. In one case, it was assumed that no combustion or mass addition occurred during the pressure transient. This resulted in a continuous decrease in chamber gas mass and pressure until ambient pressure was reached. In the second case, it was assumed that combustion occurred during the pressure transient at a rate consistent with the pressure dependence observed with the strand burner until a new equilibrium pressure was reached. Thus, the calculated pressure decay transients represent the extremes in pressure variation that should be encountered. It can be seen that the measured pressure transients fell within these calculated limits. The difference between the measured rate of decay and that calculated for continued combustion indicates that the propellant burning rate was somewhat lower than the normal steady-state rate during the pressure transient. It can also be seen that a reduction in burning rate was obtained during the early stages of the pressure drop whether the propellant was eventually extinguished or not. Similar qualitative results were obtained with other propellant compositions. This interference with the propellant burning rate is in accord with the reduction in gas-phase chemical rate that was indicated in the investigation of reference 1 by a sharp drop in combustion luminosity during the early phase of the pressure drop. This propellant-burning-rate response to rapid pressure decrease is probably partly responsible for the reduction in burning rate that has been observed at the pressure antinode during oscillatory combustion (refs. 2 and 3).

The effect of initial chamber pressure on τ for an aluminized and a non-aluminized propellant is shown in figure 3. The value of τ was relatively

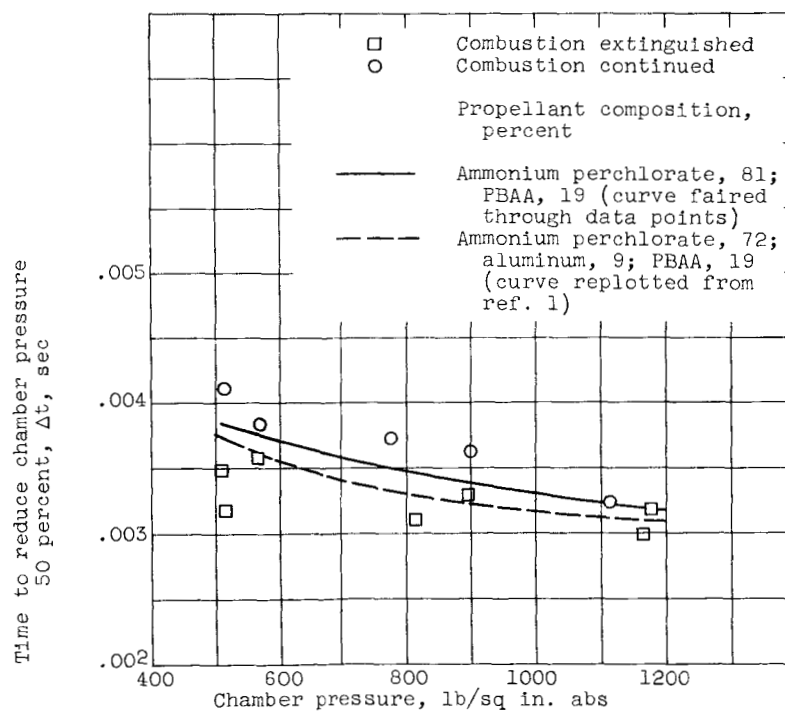Figure 3. - Comparison of effect of chamber pressure on maximum time required to reduce chamber pressure 50 percent and extinguish combustion, τ, for aluminized and nonaluminized propellant.

insensitive to chamber pressure, as evidenced by the moderate decrease with in-creasing chamber pressure and the leveling off at higher pressures. Both propel-lants showed similar trends.

The influence of aluminum and ammonium perchlorate concentration on τ is shown in figure 4. A sharp reduction in τ was noted as the concentration of ammonium perchlorate was increased by replacing binder (constant aluminum concen-tration). Adding aluminum to the propellant by replacing binder (holding ammo-nium perchlorate concentration constant) also sharply reduced τ. The added aluminum had a slightly greater effect than the ammonium perchlorate, particu-larly as the concentration of ammonium perchlorate was increased. A reduction in binder concentration by adding either aluminum or ammonium perchlorate raised the flame temperature of the propellant. This is indicated by the constant-gas-temperature lines in figure 4. A trend of decreasing τ with increasing flame temperature was suggested for these data.
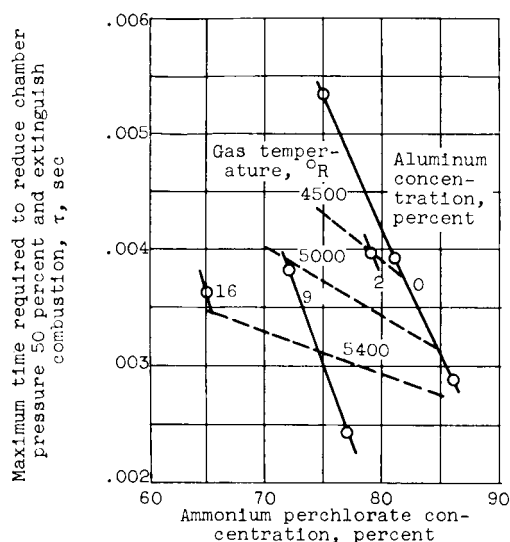

Figure 4. - Effect of aluminum and ammonium perchlorate con-centration on maximum time required to reduce chamber pressure 50 percent and ex-tinguish combustion τ. Chamber pressure, 500 pounds per square inch absolute.
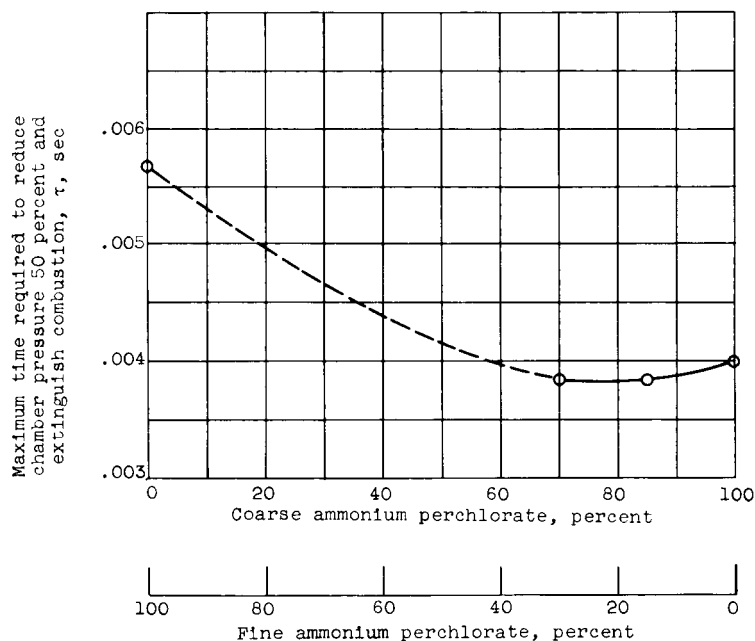

Figure 5. - Effect of ammonium perchlorate particle size on maximum time required to reduce chamber pressure 50 percent and extinguish combustion, τ. Chamber pressure, 500 pounds per square inch abso-lute; propellant composition, percent: ammonium perchlorate, 72; aluminum, 9; PBAA, 19.

The influence of average ammonium perchlorate particle size on τ is shown in figure 5. Average particle size was varied by blending coarse (89-micron) ammonium perchlorate powder with a finer (11-micron) powder. The value of τ was increased about 48 percent as the average particle size was decreased by

changing from a 70-percent-coarse - 30-percent-fine blend to a 100-percent-fine powder. No significant effect was apparent between a 70-percent-coarse - 30-percent-fine blend and a 100-percent-coarse powder. Reference 4 states that the oxidizer particle size significantly influenced the degree of aluminum agglomeration occurring on the propellant surface. Therefore, it is uncertain whether this influence on τ was due to oxidizer particle size exclusively or whether it was associated with aluminum agglomeration.

A comparison was also made between two types of binders: an epoxy-cross-linked copolymer of butadiene and a carboxylic monomer (PBAA) and a polyurethane (PU). The measured values of τ at a chamber pressure of 500 pounds per square inch absolute for a propellant containing 72 percent ammonium perchlorate, 9 percent aluminum, and 19 percent of either PBAA or PU binder (table I) were 0.0038 and 0.0037 second, respectively. The apparent insensitiveness of τ to binder type was probably a result of the relatively similar physical and chemical characteristics of composite-type binders.

The effect of several propellant components and additives on τ is indicated in table II. A propellant composition of 81 percent ammonium perchlorate and 19 percent PBAA binder was used as a basis for comparison. The various

TABLE II. - EFFECT OF SEVERAL

PROPELLANT COMPONENTS

ON τ^{a}

Substance added to reference propellant		τ, sec	Percent change from reference propellant
Type	Weight percent		
None (reference propellant)[b]		0.0039	0
Ammonium perchlorate	3	0.0033	-15
Aluminum	3	0.00325	-17
Aluminum oxide (coarse)	3	0.00255	-35
Aluminum oxide (fine)	3	0.00265	-32
Potassium fluoride (coarse)	3	0.0037	-5
Potassium fluoride (fine)	3	0.0051	+31

[a]Maximum time required to reduce chamber pressure by 50 percent and extinguish combustion.

[b]Reference propellant: 81 percent ammonium perchlorate; 19 percent PBAA binder plus additive.

components were added to the propellant by reducing the binder concentration. The addition of ammonium perchlorate, aluminum, or aluminum oxide significantly decreased τ. Conversely, it can be concluded that the addition of binder with respect to these components will increase τ. Aluminum oxide produced the largest decrease (35 percent) and showed a small effect on particle size. Only the addition of finely ground potassium fluoride caused any increase in τ, that is, any reduction in the chamber-pressure decay rate required to extinguish combustion.

DISCUSSION OF RESULTS

Since a wide variation in energy content or flame temperature was encountered when propellant composition was varied, it was interesting to observe whether any correlation between flame temperature and τ existed. It was noted that an increase in aluminum or ammonium perchlorate concentration decreased τ and, at the same time, increased the flame temperature. The addition of aluminum oxide or an increase in the particle size of the ammonium perchlorate also diminished τ substantially, but would not be expected to change the flame temperature. Preliminary results with a very high flame temperature double-base propellant have shown that τ was very high. The contradictory nature of these results precludes conclusions concerning any relation between τ and flame temperature; however, these observations do indicate that factors other than flame temperature exerted a greater influence on τ.

Variation in propellant composition also led to considerable variation in propellant-strand burning rate, but a comparison of the initial propellant burning rate (at 500 lb/sq in. abs) with τ did not reveal any apparent relation. A similar conclusion was evident if an average value of the burning rate for the range of pressure variation encountered (500 to approx. 100 lb/sq in. abs) was considered. Accordingly, it was concluded that the propellant burning rate or the burning-rate exponent n does not significantly affect the extinguishing process.

The mechanism by which aluminum oxide influences the extinguishing process probably is physical rather than chemical by reason of its high chemical stability. Adding potassium fluoride to the propellant produced an interesting effect on τ. This additive was the only one (except for the binder) that showed any tendency to increase τ, that is, make extinction easier. A strong effect of potassium fluoride particle size was indicated by the larger τ value that resulted from the smaller particle size. The influence of potassium fluoride on τ may be the result of the chemical inhibiting effect postulated for alkali-metal halide salts in reference 5.

The effects of propellant composition on τ can be explained qualitatively in terms of the behavior of propellant surface temperature during the decay process. The autoignition temperature varies from 450° to 650° F for a wide range of propellants. Local surface temperature during steady combustion is reported to be approximately 1800° F (ref. 6). It appears plausible, therefore, to

8

assume that extinction will occur when the venting rate is sufficiently high to reduce the surface temperature by 1200° to 1400° F. According to reference 7, a heat balance at the surface of the propellant illustrates the factors that influence the surface temperature during steady burning:

$$\dot{m}\left[C_s(T_s - T_0) - Q_s\right] = \lambda_g \frac{T_c - T_s}{L}$$

where $\dot{m}$ is the average mass burning rate, C_s is the average propellant heat capacity, T_s is the average surface temperature, T_0 is the initial temperature, Q_s is the average heat of pyrolysis of the propellant (negative for an endothermic process), λ_g is the average thermal conductivity of the gas, T_c is the combustion temperature, and L is the flame thickness (defined as the distance from the propellant surface to the point where the reaction is completed). The right side of the equation represents the heat conducted from the combustion products to the propellant surface, while the left side represents the heat required to heat and gasify the propellant components. It can be seen from this equation that the feedback of heat from the combustion process must be interrupted during the venting process in order to cool the surface of the propellant. Some decrease in the heat conduction results from the reduction in gas combustion temperature T_c due to the expansion; however, this reduction is relatively small, even for large changes in pressure, and consequently any substantial effect on the heat transferred must come from an abnormal increase in flame thickness. It is therefore assumed that the flame thickness L must be an inverse function of Δt (time to reduce chamber pressure 50 percent); then as Δt is decreased, the flame thickness will increase and thereby diminish the heat conducted to the surface. The cooling of the surface will then result primarily from the heat absorbed during continued pyrolysis of the hot binder because the only component of the propellant that pyrolyzes endothermically (negative Q_s) is the binder. The decomposition of the ammonium perchlorate during the pressure transient is assumed to be exothermic since it is self-sustaining, as indicated in reference 8. Therefore, the higher the binder concentration, the greater the heat absorption capacity of the decomposition products. Thus a smaller disturbance in heat conduction (larger τ) should be required to decrease the surface temperature below its autoignition point. The experimental results are in agreement with this conclusion since it was observed that higher binder concentrations increased τ. It is also apparent that heated particles at the propellant surface such as aluminum and aluminum oxide will have varying cooling rates. Aluminum oxide will cool more slowly because of its relatively poor thermal conductivity and should, therefore, require a smaller value of τ to extinguish combustion. It was found that τ was lower for propellants containing aluminum oxide than for those containing equivalent quantities of aluminum. The particle size will also affect its rate of cooling as well as the length of time the particle remains attached to the propellant surface. Thus, among particles heated to the same temperature, τ should be smallest for the largest particles because they will cool more slowly and will remain in contact with the propellant longer. This trend was observed experimentally.

SUMMARY OF RESULTS

The effect of variation in propellant composition on the extinction of combustion by a rapid pressure decrease was substantial. When the concentrations of components such as aluminum, ammonium perchlorate, and aluminum oxide were increased, the propellant was more difficult to extinguish, whereas the binder and finely ground potassium fluoride produced an opposite effect. The ease with which solid-propellant combustion may be extinguished was strongly dependent on physical factors such as the average particle size and the thermal conductivity of solid particles contained in the propellant. Examination of the data also indicated no significant correlation between extinguishability and propellant burning rate.

Lewis Research Center
  National Aeronautics and Space Administration
    Cleveland, Ohio, September 22, 1962

APPENDIX - METHOD OF CALCULATING CHAMBER-PRESSURE DECAY

The variation of chamber pressure with time can be represented by the following differential equation:

$$\frac{dP}{dt} = \frac{RT}{V} \frac{dm}{dt}$$

where P is the chamber pressure, t is time, R is the gas constant, T is the absolute gas temperature, V is volume, and m is chamber gas mass. This equation neglects the small change in chamber volume with time resulting from combustion of the propellant and assumes that the gas temperature remains constant. The rate of change of mass dm/dt is equal to the rate of mass addition due to combustion minus the rate of mass discharge. The rate of mass addition is equal to

$$r\rho S = KP^n\rho S$$

where r is the propellant burning rate, ρ is the propellant density, S is the burning surface area, and K and n are constants. The rate of mass discharge through a sonic flow nozzle is equal to

$$PA_tC_D = PA_tg\gamma \frac{\sqrt{[2/(\gamma + 1)]^{(\gamma+1)/(\gamma-1)}}}{\sqrt{g\gamma RT}}$$

where A_t is the nozzle flow area, C_D is the nozzle discharge coefficient, g is a conversion constant, and γ is the ratio of specific heats. Substitution of these relations in the expression for dm/dt yield

$$\frac{dP}{dt} = \frac{RT}{V} (KP^n\rho S - PA_tC_D)$$

Integration over the range P to P_0 (the initial pressure when t = 0) gives the relation

$$t = \frac{V}{RT} \frac{1}{C_DA_t} \frac{1}{n-1} \log e \left(\frac{1 - \frac{C_DA_t}{K\rho S} P^{1-n}}{1 - \frac{C_DA_t}{K\rho S} P_0^{1-n}} \right)$$

The variation of chamber pressure with time without mass addition can be represented by the differential equation

$$V \frac{1}{\gamma} P^{(1-\gamma)/\gamma} \frac{dP}{dt} = \frac{RT_0}{P_0^{(\gamma-1)/\gamma}} \frac{dm}{dt}$$

where the adiabatic temperature relation has been assumed and the subscript 0 refers to initial or starting conditions. In this case,

$$\frac{dm}{dt} = -PA_t C_D$$

Therefore,

$$V \frac{1}{\gamma} P^{(1-\gamma)/\gamma} \frac{dP}{dt} = - \frac{RT_0}{P_0^{(\gamma-1)/\gamma}} PA_t C_D$$

Substitution for the nozzle discharge coefficient

$$C_D = g\gamma \frac{\sqrt{[2/(\gamma + 1)]^{(\gamma+1)/(\gamma-1)}}}{\sqrt{g\gamma RT}}$$

and substitution of the adiabatic relation for the chamber gas temperature T give

$$-V \frac{1}{\gamma} \frac{P_0^{(\gamma-1)/\gamma}}{RT_0 A_t} \frac{\sqrt{\dfrac{T_0}{P_0^{(\gamma-1)/\gamma}}} \sqrt{g\gamma R}}{g\gamma \sqrt{[2/(\gamma + 1)]^{(\gamma+1)/(\gamma-1)}}} P^{(1-3\gamma)/2\gamma} dP = dt$$

Integration with $P_0 = P$ when $t = 0$ results in the final expression

$$t = \frac{-2V}{1 - \gamma} \frac{P_0^{(\gamma-1)/2\gamma}}{\sqrt{\gamma g R T_0}} \frac{1}{A_t} \frac{1}{[2/(\gamma + 1)]^{(\gamma+1)/(2\gamma-2)}} \left[P^{(1-\gamma)/2\gamma} - P_0^{(1-\gamma)/2\gamma} \right]$$

For the case that considers combustion during the pressure drop the accuracy of the calculation is greatest for high chamber pressures since the burning rate was extrapolated for pressures below 400 pounds per square inch absolute. This extrapolation probably accounted for part of the observed differences between measured and calculated terminal equilibrium pressures for conditions that did not extinguish the propellant burning.

REFERENCES

1. Ciepluch, Carl C.: Effect of Rapid Pressure Decay on Solid Propellant Combustion. ARS Jour., vol. 31, no. 11, Nov. 1961, pp. 1584-1586.

2. Horton, M. D.: One-Dimensional Solid Propellant Oscillatory Burner. ARS Jour., vol. 31, no. 11, Nov. 1961, pp. 1596-1597.

3. Crump, J. E., and Price, E. W.: Effect of Acoustic Environment on the Burning Rate of Double-Base Solid Propellants. ARS Jour., vol. 31, no. 7, July 1961, pp. 1026-1029.

4. Povinelli, L. A., and Ciepluch, C. C.: Surface Phenomena in Solid Propellant Combustion. Paper presented at JANAF-ARPA-NASA Solid Propellant Group Meeting, Pittsburgh (Penn.), June 5-7, 1962.

5. Friedman, Raymond, and Levy, Joseph B.: Survey of Fundamental Knowledge of Mechanisms of Action of Flame-Extinguishing Agents. TR 56-568, WADC, Jan. 1957.

6. Andersen, W. H., et al.: A Model Describing Combustion of Solid Composite Propellants Containing Ammonium Nitrate. Combustion and Flame, vol. 3, no. 3, Sept. 1959, pp. 301-317.

7. Sumerfield, Martin, et al.: Burning Mechanism of Ammonium Perchlorate Propellants. Prog. in Astronautics and Rocketry. Vol. 1. Solid Propellant Rocket Res., Academic Press, 1960, pp. 141-182.

8. Friedman, Raymond, Levy, Joseph B., and Rumbel, Keith E.: The Mechanism of Deflagration of Pure Ammonium Perchlorate. TN-59-173, Atlantic Res. Corp., Feb. 5, 1959.